# Potato Peel Waste: Stability and Antioxidant Activity of a Freeze-Dried Extract

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## ABSTRACT

Aqueous extracts of potato peel waste were freeze-dried. High performance liquid chromatography (HPLC) of the freeze-dried extracts revealed that chlorogenic (50.31%), gallic (41.67%), protocatechuic (7.81%), and caffeic (0.21%) acids were the major phenolics. During 15 days storage of the freeze-dried extract, no degradation of phenolics occurred. After 4 days storage at 63°C, 5.00g of sunflower oil containing either the freeze-dried extract (200 ppm) or butylated hydroxyanisole (BHA) (200 ppm) reached peroxide values (PV) of 37.38 and 37.47 meq $kg^{-1}$ respectively. L-ascorbic acid-6-palmitate was the best antioxidant (PV= 10.65 meq $kg^{-1}$) but the freeze-dried extract was as good as BHA.

Key Words: freeze-dried, potato extract, chlorogenic acid, lipid peroxidation

## INTRODUCTION

FOOD PHENOLIC ANTIOXIDANTS, such as butylated hydroxyanisole (BHA), tert-butylated hydroquinone, and propyl gallate, are used as antioxidants in foodstuffs against oxidative rancidity (Cuvelier et al., 1992). Such antioxidants are used, but many questions regarding human health effects related to them are unresolved. Also general public concern exists regarding food additives and their safety.

Some components of extracts isolated from plant materials have been proven in model systems, to be as effective antioxidants as synthetic antioxidants (Pratt and Watts, 1964; Hayase and Kato, 1984; Fukuda et al., 1985; Loliger, 1989; Pratt and Hudson, 1990; Papadopoulos and Boskou, 1991). Potato peel contains phenolic acids. The largest portion consists of chlorogenic acid (CGA). Other phenolics, gallic acid (GAC), caffeic acid (CFA), and protocatechuic acid (PCA), are present in potato peel in low amounts (Lisinska and Leszczynski, 1987). The possibility exists for utilizing a waste, i.e., potato peel, a source for a useful product for the food industry. Many naturally occurring phenolic compounds have antioxidant activity. Our objective was to evaluate a freeze-dried water extract of potato peel waste, for its stability during storage and to compare its antioxidant activity with commercially available antioxidants.

## MATERIALS & METHODS

### Reagents

Methanol (MeOH) and chloroform were purchased from Fisher Chemical Company (Pittsburgh, PA). Soluble starch, sodium thiosulfate, potassium iodide (KI), and glacial acetic acid (HAc) were purchased from Baxter Scientific Products (Minneapolis, MN). CGA, PCA, GAC, CFA, BHA and l-ascorbic acid-6-palmitate, (ASC) were purchased from Sigma Chemical Company (St. Louis, MO).

### Potato peel waste and sunflower crude oil

Potato peel waste was obtained from Simplot Food Division (Grand Forks, ND), and samples were prepared following procedures used by Rodriguez de Sotillo et al., 1994. Freshly extracted sunflower seed crude oil (SFO) samples were obtained in 4 L containers from Cargill Seed Oil Company (West Fargo, ND). Following delivery, the oil was cooled at 4°C for 4 hr. After cooling, nitrogen was bubbled through the oil for 5 min. to minimize oxidation, and the oil was then stored at −12°C until analyzed.

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### HPLC analysis

The HPLC instrument included a 501 HPLC pump from Waters Millipore (Mildford, MA), an injector (Rheodyne Co., Catati, CA), a guard column (3 mm i.d. × 22 mm) containing C18/Corasil, a 3.9 mm × 30 cm μBondapak $C_{18}$™ column, a 440 absorbance detector with 313 nm filter, and a Data Module from Waters Millipore (Mildford, MA). The mobile phase Water:MeOH:HAC (64:35:1 v/v/v), was delivered isocratically at 1 mL/min., and the effluent monitored at 313 nm. In triplicate, solutions containing up to 80 μg/mL of CGA, PCA, GAC, and CFA were injected into the HPLC system, and standard curves were prepared. A 10 μL aliquot of a reconstituted portion of potato peel waste freeze-dried extract (EXT) in water was analyzed by HPLC (Rodriguez de Sotillo et al., 1994). Major peaks were identified by co-migration with phenolic acid standards.

### Preparation of freeze-dried extract

Triplicate 5-g samples of potato peel waste were extracted using the reflux method (Rodriguez de Sotillo et al., 1994), and 10 μL of supernatant were analyzed by HPLC for phenolic acid content. The remaining filtrates were kept in a freezer at −12°C overnight, and immediately freeze dried at 70 mtorr vacuum and −60°C for 3 days in a Dura-Dry Freeze-dryer (FTS Systems, Inc. Stone Ridge, NY). Samples were removed from the freeze drier, and were ground with a mortar and pestle. From each freeze-dried sample, a 0.05 g sample was reconstituted in 10 mL water, and a 10 μL aliquot was analyzed by HPLC for phenolic acid. Major peaks were identified by co-elution with pure samples of phenolic acids, and quantified using standard curves. The remaining freeze-dried samples were stored tightly capped in plastic vials at room temperature (~23°C) until tested as an antioxidant in SFO.

### Stability of potato peel waste freeze-dried extract

Triplicate 60-g samples of potato peel waste were extracted using the water reflux method (Rodriguez de Sotillo et al., 1994) with modifications in the solvent volume, time for homogenization, and refluxing period. The filtrate was frozen at −12°C for 2 days, and freeze-dried as described. An aliquot (0.05g) was weighed, mixed with 10 mL water using a Vortex-Genie 2™ Mixer, for 4 min, and 10 μL were analyzed for phenolic acid by HPLC. The remaining freeze-dried sample was divided into two 5-g aliquots and kept in plastic vials, one stored at ambient (~23°C) temperature, and the other at 4°C. Daily for 15 days, 0.05g from each vial was reconstituted in 10 mL water, mixed for 4 min, and 10 μL aliquots of reconstituted solutions were analyzed by HPLC for phenolic acids.

### Evaluation of antioxidant activity

To determine antioxidant activity solutions containing 200 ppm of the following compounds were prepared in SFO: BHA, the freeze-dried extract (EXT), ASC, CGA, GAC and a mixture (MXT) of phenolic acids identified in the extract. Triplicate portions of each solution (50 g) were incubated in a Blue M Stable-Therm 108 oven, thermostatically controlled at 63°C, for 4 days. Antioxidant activities and peroxide values of selected antioxidants in the stored oil samples were determined by official AOAC (1990) method No. 965.33 for peroxide value of oils and fats. A portion of the oil (5g ± 0.05) from a stored sample was treated by addition of 30 mL of a solution of $CH_3COOH$:$CHCl_3$ (3:2, v/v) and

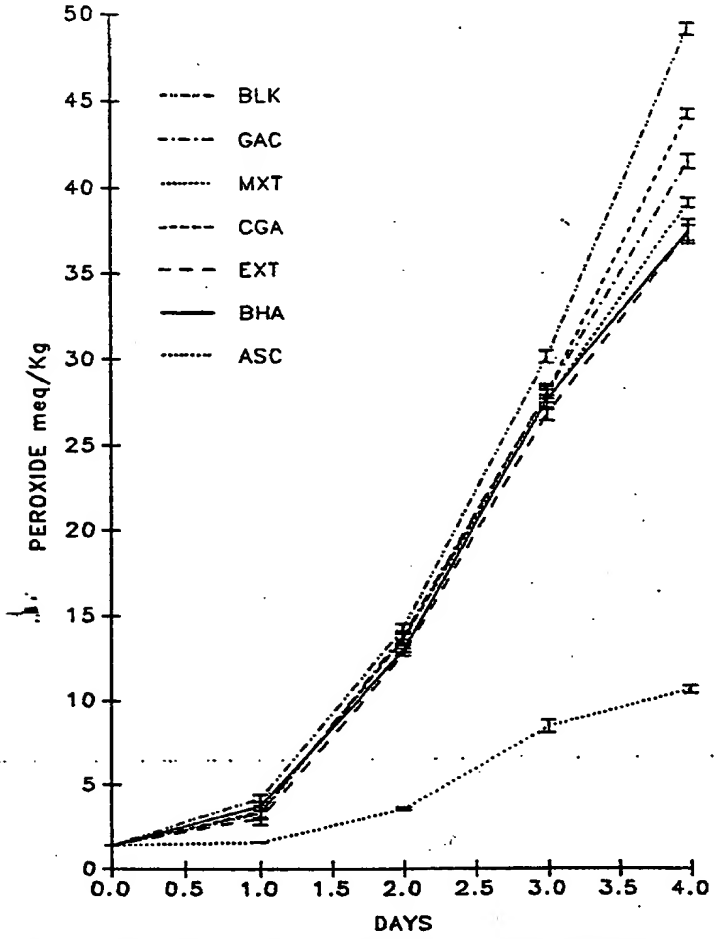


**Fig. 1—Effect of antioxidants at 200 ppm on the stability of sunflower seed crude oil stored at 63°C. Samples: without antioxidant=BLK; containing: gallic acid=GAC, synthetic mixture of phenolic acids=MXT, chlorogenic acid=CGA, potato peel freeze-dried extract=EXT, butylated hydroxyanisole=BHA, and L-ascorbic acid-6-palmitate= ASC.**

30 mL water, and, after addition of 0.5 mL of a KI saturated solution, titrated with 0.1N $Na_2S_2O_3$ using 0.5 mL of 1% starch solution as indicator.

### Statistical analyses

The general linear model (GLM) program for analysis of variance and regression estimation of the Statistical Analysis Systems (SAS Institute, Inc., 1985) were used to analyze data.

## RESULTS & DISCUSSION

### Phenolic acids in the extract

Prior to freeze-drying, the concentration of the phenolic acids identified in the potato peel waste liquid extract in mg/g of potato peel waste was: CGA= 0.30, GAC= 0.13, PCA= 0.04, and CFA= 0.01. The concentrations of the phenolic acids CGA, GAC, PCA, and CFA in the freeze-dried extract, (mg/g extract) were 4.83±0.42, 4.00±0.07, 0.75±0.04, and 0.02±0.00, respectively. The amount of freeze-dried extract/5 g of potato peel waste was (0.28 ± 0.01)g. Chlorogenic acid, GAC, PCA, and CFA constituted 62.50%, 27.08%, 8.33%, and 2.08%, respectively, of the total phenolic acids from the liquid extract. In the freeze-dried extract they constituted 50.31%, 41.67%, 7.81%, and 0.21%, respectively. The percentage of GAC increased by about one-third while the percentage of CFA decreased, in the freeze dried extract. The differences in percentages between the liquid and the freeze-dried extracts for both GAC and CFA were probably due to degradation of CFA into GAC during freeze-drying. This hypothesis is supported by Gross (1992), who emphasized that hydroxybenzoic acids result from the side chain degradation of cinnamic acids. He suggested that the degradative sequence reactions for CFA occurs as CFA→PCA→GAC.

### Stability of the freeze-dried extract

HPLC analysis of an aliquot of EXT was conducted on day 0. The CGA, GAC, PCA, and CFA of the EXT on day 0 were 4.89±0.58, 4.49±0.23, 0.79±0.09, and 0.03±0.01 mg/g extract. Chromatographic analysis of stored samples over a 15-day period on aliquots of EXT showed four phenolic acids CGA, GAC, PCA, and CFA. Concentrations of these acids in samples stored at 4°C and 25°C did not differ from day 0 to day 15, ($P>0.05$). However, when the stability of potato peel waste liquid extracts stored at 25°C had been determined (Rodriguez de Sotillo et al., 1994) differences occurred in the concentrations of phenolic acids after the first day of storage.

### Antioxidant activity

The initial PV for freshly extracted SFO on day zero was 1.39 ± 0.00 meq/kg oil. The PV's of SFO samples containing 200 ppm BHA, ASC, GAC, CGA, EXT, MXT, as well as an untreated SFO sample (BLK), after 4 days incubation at 63°C were 37.47±0.72, 10.65±0.21, 41.53±0.44, 44.29±0.30, 37.38±0.46, 39.17±0.30, and 49.15±0.36, respectively. The PV's increased in the order ASC<EXT<BHA<MXT<GAC<CGA.

A plot of PV vs time was constructed (Fig. 1), and, indicated that after 4 days, the PV had changed in BLK by >40 meq/Kg. A steady increase in PV occurred with time (Fig. 1). ASC was most effective in retarding the elevation of PV, and was significantly different ($P<0.05$) from the other antioxidants studied. These results agreed with those of Cort, (1974) who reported that ASC had a better protective activity than BHA at levels of 100 ppm in soybean oil using the Schaal Oven M thod Test (Eastman Chemical Products, 1987).

The PV's of SFO samples stored 4 days at 63°C containing EXT were not significantly different ($P>0.05$) from those stored under the same conditions containing BHA. Thus the antioxidant efficiency of EXT was about equivalent to that of BHA. Cuvelier et al. (1992) reported a comparative study of antioxidant efficiency of some acid phenols including CGA, GAC, PCA, CFA, as well as BHA. They found the antioxidant activity in methyl linoleate to be GAC>CFA>PCA>BHA>CGA. However, in our investigation, the antioxidant activity of BHA was greater than both CGA and GAC. This difference may have been due to differences in solubility of GAC and BHA in the different oil substrates used.

The least antioxidant activity was observed with CGA and GAC and MXT, which simulated EXT, was third best. The EXT may have contained substances which not identified which were antioxidants or acted as synergists to increase the effectiveness of EXT as an antioxidant.

The best antioxidant activity was with ASC. This may have been due to its increased solubility in SFO, to the ability of ASC to act as reducing agent or oxygen scavenger, or possibly the ability to act in combination with tocopherols in the SFO. Gordon (1990) reported that ASC acts by decomposing lipid peroxidation products into non-radicals. Its marked antioxidant activity may be due to its efficiency in regenerating tocopherol by reducing the tocopheroxyl radical.

The solubilities f the antioxidants varied, and this may in part, account for differences in peroxide values.

The usefulness of EXT as an antioxidant, would depend on its solubility. Phenolics have low solubility in oils which may be a disadvantage. However, the antioxidant activity of cinnamic acids can also be explained by their ability to accept free radi-

cals, chelation properties, and effectiveness against lipoxygenase catalyzed reactions. Two or more extracted components may interact to produce an antioxidant effect. The antioxidant activities of potato peel freeze-dried extract probably occurs by several mechanisms of action. Thus, low solubility would not necessarily preclude the extract's potential as an antioxidant.

## CONCLUSION

THE ORDER OF ANTIOXIDANT ACTIVITY we found was ASC>EXT>BHA>MXT>GAC>CGA, which indicates that potato peel freeze-dried extract may have a potential use as an antioxidant in foods. Further studies that are needed include toxicological effects, flavor and color effects, sensory evaluation of food products using the extract as an antioxidant, and phenolic compounds in potato tubers of different cultivars.

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